Poly(4-vinylpyridine) as ligand for Au(I) and Zn(II) cations: luminescent metal-containing polymers

Elnaz Hobbollahi¹ · Manuela List^{2,3} · Uwe Monkowius⁴

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Abstract

The poly-dentate ligand poly(4-vinylpyridine) (P4VP, $M_w \approx 60,000 \text{ g mol}^{-1}$) reacts with $(\text{Me}_2\text{S})\text{AuCl}$ or ZnCl_2 yielding white polymers with empirical formula $(\text{PVP})(\text{AuCl})_{0.4}$ and $(\text{PVP})(\text{ZnCl}_2)_{0.7}$. Upon excitation with UV light, both metal-containing materials feature luminescence. Emissions of $(\text{P4VP})\text{--AuCl}$ are based on aurophilic interactions whereas for $(\text{P4VP})\text{--ZnCl}_2$, an excitation wavelength-dependent luminescence could be observed. The latter behavior can be explained by the formation of aggregated species with different excitation energies. For comparison, the model compound $(\text{Etpy})\text{AuCl}$ (Etpy = 4-ethylpyridine) is prepared and structurally characterized. The solid-state structure reveals that no aurophilic or $\pi\text{--}\pi$ interactions are present. The compound does not show photoluminescence. The solid-state structure of the disproportionation product $(\text{Etpy})\text{AuCl}_3$ has been determined as well.

Graphical abstract

Keywords Metal-containing polymers · Gold · Zinc · UV–Vis spectroscopy · Luminescence · X-ray structure determination

Dedicated to Professor Heinz Falk on the occasion of his 80th birthday.

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✉ Uwe Monkowius
uwe.monkowius@jku.at

- ¹ Institute of Inorganic Chemistry, Johannes Kepler University, Linz, Austria
- ² Institute of Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria
- ³ Technical University of Applied Sciences Rosenheim, Campus Burghausen, Burghausen, Germany
- ⁴ Linz School of Education, Johannes Kepler University, Linz, Austria

Introduction

In the last years, research on transition metal-containing polymers increased significantly. Incorporation of transition metal ions into polymeric materials leads to a change of mechanic, electronic, optic, or magnetic properties [1–9]. Different strategies have been exploited to prepare metal-containing polymers leading to different types of polymers. In principle, the metal ions can be part of the polymeric backbone or part of the side groups. In the first case, the polymer is formed in a reaction not unlike a classical step-growth polymerization which leads to a material which most obvious term would be “coordination polymer” or in branched versions “coordination networks”. However, these terms are already occupied for material where metal ions and ligands form a polymer or network in solid state

but dissociate into its components upon dissolution—if the material is soluble at all what actually rarely is the case. On the contrary, metal-containing polymers do not disassemble in solution but stay intact in a macromolecular form. According to a convention, these polymers are referred to as type II polymers [4, 5].

Polymers with functional groups which are capable to coordinate to a metal ion form metal-containing polymers of type I [4, 5]. The variety of these groups is as large as it is the case for classical non-polymeric ligands. Although it is in principle also possible to polymerize monomeric complexes bearing a polymerizable group, maybe the easiest way to synthesize such material is the use of commercially available polymers which contain a ligand as side group. For example, a huge number of different types of polymers, e.g., polyolefins and polyacrylates, which are functionalized with carboxylates, amines, alcohols, etc. are offered by several suppliers. Conceptually, these polymers are nothing else than poly-dentate ligands.

An obvious option for a type I polymeric ligand is poly(4-vinylpyridine) (P4VP) as substituted and non-substituted pyridines are omnipresent ligands in coordination chemistry and synthetic protocols for a huge number of pyridine metal complexes are known and are often extremely simple. Indeed, P4VP has been used in several studies for the preparation of metal-containing polymers. It is soluble in polar solvents and cheap. Examples for metals which have been used are Ru, Co, Ni, Zn, Cu, Os, Fe, Sn, Al, Cr, Mn, Mo, Pd, Hg, W, Ti, and rare earth metals [10–25]. Interestingly, to our knowledge there is only one publication on a gold-containing P4VP up to now. Rawashdeh-Omary et al. synthesized P4VP–Au–C₆F₅. They characterized the material by ¹H NMR and luminescence spectroscopy. The luminescence is assigned to an excited state based on aurophilic interactions randomly formed in the polymeric materials [26].

In this contribution, we will present (P4VP)–AuCl and (P4VP)–ZnCl₂ polymers and as model compound (Etpy)AuCl (with Etpy = 4-ethylpyridine). In addition to chemical characterization, we also investigated their photophysical properties.

Results and discussion

Synthesis

The metal-containing polymers are prepared by reaction of an ethanolic solution of P4VP ($M_w = 60,000 \text{ g mol}^{-1}$) with a DCM solution of (Me₂S)AuCl (**1**, Scheme 1) and ZnCl₂ (**2**), respectively. For **1**, a molar ratio for pyridine:gold of 1:1 and for **2** an excess of 2:1 for pyridine:Zn were used. In both cases, a colorless precipitate was formed which was filtered off and dried. Under the assumption that besides AuCl and ZnCl₂

Scheme 1

no further constituents are present, the results of the C, H, N analysis indicate empirical formulas of (C₇H₇N)(AuCl)_{0.4} and (C₇H₇N)(ZnCl₂)_{0.7}.

The zinc polymer is not soluble in common organic solvents indicative of a high degree of cross-linking by the zinc cation. Zinc cations usually exist in tetrahedral coordination geometry. For zinc halide complexes, the standard composition is L₂ZnX₂ with two *N*-heterocyclic ligands L attached to the zinc cation. Hence, the Zn(II) atom can be coordinated by pyridine groups in an inter- or intrachain manner cross-linking the P4VP polymer. On the contrary, the (P4VP)–AuCl complex is soluble in DMSO allowing for recording a ¹H NMR spectrum. In Fig. 1, the proton NMR of free P4VP is depicted showing broad resonances of the pyridine protons at 6.60 and 8.28 ppm. Upon coordination to the Au(I) atom, long tails at the high-field side of the signals of the pyridine moiety appear. These results are in accordance with the homologue (P4VP)Au(C₆F₅) polymer and the model compound **3** (vide infra) [26].

A *para*-substituted ethylpyridine can be regarded as a small molecule analog for P4VP. The model compound (Etpy)AuCl (**3**) will allow photophysical investigation of the pyridine–gold moiety also present in P4VP. Particularly, it can help to answer the question if luminescence is based on the isolated moiety or on an aggregation by π – π or aurophilic interactions. **3** was prepared from (Me₂S)AuCl with 4-ethylpyridine in DCM. Interestingly, the slightly less reactive (tht)AuCl (tht = tetrahydrothiophene) does not give **3** as only the gold precursors can be isolated upon reaction with Etpy. The ¹H NMR spectrum of **3** is as expected for an AA'BB' spin system substituted with an ethyl group and corresponds also to the resonances of polymer **1**.

Structural studies

Crystals of **3** suitable for single-crystal X-ray diffraction were obtained by gas phase diffusion of diethyl ether into a solution of **3** in DCM at 4 °C. **3** crystallizes in the monoclinic space group *P*2₁/*c* with *Z* = 4. Interestingly, neither aurophilic contacts nor π – π stacking interactions are present. The shortest Au–Au distance is 3.962 Å and well beyond

Fig. 1 Excerpt of the ^1H NMR spectra of the free P4VP (bottom) and **1** (top) in $\text{DMSO}-d_6$

the accepted limit for aurophilic interactions. The gold atom is linearly coordinated by the nitrogen and chlorine atoms with an N–Au–Cl angle of $177.7(2)^\circ$ (Fig. 2). The Au–Cl and Au–N distances are $2.248(3)$ and $2.025(8)$ Å, respectively. These values are in accordance with reported values for py–Au–Cl [27, 28]. It should be noted that two forms of gold chloride complexes bearing various pyridine ligands are known. In their crystals, they are either found as neutral molecule py–Au–Cl as it is the case for **3** or in the ionic form $[(\text{py})_2\text{Au}][\text{AuCl}_2]$ [27–32]. The formation is dependent on the crystallization conditions and the pyridine ligand and has some relevance also for the structure of **1**. However, we tried to recrystallize **3** in different solvents but we only could isolate the neutral form. Hence, it is tempting to postulate that **1** is also neutral.

Only a few red crystals of **4** were obtained from one attempt to grow crystals of **3**. Obviously, it is formed by a disproportionation reaction as also some violet precipitate was formed. The latter is indicative of elemental gold. As it was not the goal of this study to synthesize pyridine–gold(III) complexes, no attempts to prepare pure **4** were undertaken. For a proper chemical analysis, the

amount of formed materials was too low. However, we include the molecular structure for completeness and due to the fact that L–AuCl₃ complexes bearing pyridine-like ligands L are relatively rare [33–38]. **4** crystallizes in the orthorhombic space group *Pcab* with eight formula units in the unit cell. The gold atom is surrounded by the nitrogen atom of the pyridine ligand and three chlorido ligands in a quadratic–planar coordination environment with an angular sum of exact 360.0° (Fig. 3). With $2.030(6)$ Å, the Au–N distance is slightly longer than in **3**, as it is the case for the Au–Cl distances which are between $2.260(2)$ and $2.277(2)$ Å (Table 1). These values are comparable to those reported [33–38]. In addition, there are long Au $\cdots$ Cl contacts of $3.275(2)$ and $3.408(2)$ Å between the Au(III) atom and two chlorine atoms of two neighboring complexes forming an infinite chain (Fig. 3). These values are slightly below the sum of the van der Waals radii of Au (1.66 Å) and Cl (1.75 Å) of 3.41 Å. Considering these interactions, the gold atom exists in a sixfold coordination environment which is not unprecedented but relatively rare for Au(III) atoms [37, 39–44]. Between the pyridine moieties short π – π stacking interactions of ~ 3.6 Å are found.

Fig. 2 Molecular structures of **3** and **4** (displacement ellipsoids drawn at the 50% probability level, H atoms as spheres with arbitrary radii)

Fig. 3 Excerpt from the cell plot of **4** showing Cl...Au contacts

Photophysical studies

In the solid state, both metallo-polymers clearly feature luminescence upon excitation with UV light. P4VP, however, is only very weakly emissive at 77 K ($\lambda_{\text{max}} \sim 430$ nm). At room temperature, no authentic emission could be detected. This behavior is not surprising as it is similar to pyridine which is considered to be almost non-emissive in solution, because low-lying $n-\pi^*$ states efficiently quench emissions. At 77 K, pure crystalline pyridine as well as solutions of pyridine feature weak dual emission with a broad, structureless phosphorescence band (360–540 nm, $\lambda_{\text{max}} \sim 430$ nm) [45]. In the case that the $n-\pi^*$ transition is blocked by protonation, a broad phosphorescence band could be detected around 400 nm even at room temperature in solution [46]. The emission of both the free pyridine as well as of the pyridinium cation was assigned to a $^3\pi-\pi^*$ excited state. Just recently, we have reported on nicotine–zinc halide complexes which feature phosphorescence in solid state at 77 K comparable to

the pyridinium cation [47]. Nicotine is a naturally occurring pyridine derivative.

The P4VP–gold complex is soluble in DMSO but not in other common organic solvents. This fact prevents a detailed investigation of the photophysical properties in solution because DMSO absorbs already at ~ 300 nm. In solid state, the P4VP–gold complex shows intense emissions at ~ 490 nm both at room temperature as well as at 77 K (Fig. 4). In principle, the emission can either be based on excited states based on aurophilic interactions or on an intraligand (IL) excited state of the pyridine moiety as described above. For this reason, we investigated the luminescence behavior of the mono-nuclear complex **3** as a model. It is particularly helpful that according to the crystal structure, no close aurophilic or $\pi-\pi$ interactions are present between the complexes. Therefore, emissions based on intermolecular interactions are not likely in solid state. Indeed, we could not detect authentic emissions either in solution or in solid at r.t. or 77 K. This observation is also in accordance with the absence of luminescence of py–Au–Cl reported previously [29]. As there are no clear and intense emissions associated with the molecular entity ‘py–Au–Cl’ in **3**, we tentatively assign the emission band of the polymer **1** to excited states related to aurophilic interactions comparable to P4VP–Au–C₆F₅ reported by Rawashdeh-Omary et al. [26] and other pyridine–gold(I) complexes featuring close Au–Au contacts in the solid state [29, 31]. These interactions can be either intra- or interchain. However, for (P4VP)Au(C₆F₅) both the intensity as well as the emission wavelength are strongly dependent on the temperature and excitation wavelength. We could not detect a comparable behavior for **1**. Due to insolubility of **1** in standard ‘spectroscopic’ solvents, no absorbance spectra could be recorded. The excitation spectra of neat **1** feature low-energy bands at $\lambda_{\text{max}} = 350$ nm (r.t.) and below 350 nm (77 K). The free P4VP has an absorbance at 254 nm, complex **3** one of 243 nm each in DCM solution. Therefore, the bands in the excitation spectra could not be assigned to $\pi-\pi^*$ transition of the pyridine moiety. In fact, these values are in the standard range of other complexes with aurophilic contacts in the solid state [31, 48, 49]. Complex **4** absorbs at 243 and 316 nm. The low-energy band is typical for a Cl→Au ligand-to-metal charge transfer (LMCT) [50].

As already mentioned, some pyridine derivatives show photoluminescence upon blocking its quenching $n-\pi^*$ states. As demonstrated above for **3**, not every Lewis acidic centers lead to emissive pyridine moieties. However, compound **2** is emissive in solid state both at room temperature and at 77 K. The emission spectra are highly dependent on the excitation wavelength. However, no systematic dependency between excitation wavelength and emission spectra could be identified. In Fig. 5, only one example is depicted. All emission bands are relatively broad covering a large fraction of the

Table 1 Bond lengths/Å and angles/° for **3** and **4**

	3	4
Au1–N1	2.025(8)	2.030(6)
Au1–Cl1	2.248(3)	2.266(2)
Au–Cl2	–	2.277(2)
Au–Cl3	–	2.260(2)
N1–Au1–Cl1	177.7(2)	179.1(2)
N1–Au1–Cl2	–	89.7(2)
N1–Au1–Cl3	–	88.8(2)

Fig. 4 Electronic spectra of **1** in solid state: **a** absorption spectrum of free P4VP in DCM ($c = 5 \times 10^{-5}$ mol dm $^{-3}$); **b** emission spectra at r.t. and **c** 77 K ($\lambda_{\text{exc}} = 350$ nm); **d** excitation spectra at r.t. and **e** 77 K ($\lambda_{\text{det}} = 450$ nm)

visible spectral region and show more than one maximum. This observation is similar not only to (P4VP)Au(C $_6$ F $_5$) but also resembles the emission behavior of imidazolium-based ionic liquids. Like pyridinium, the imidazolium cation is a six-electron π system. The unusual luminescence properties have been explained by the existence of aggregated species which give rise to energetically different excited (and emissive) states with inefficient excitation energy-transfer process between them [51–54]. In an analogous interpretation, the zinc cations in P4VP might impose aggregation of pyridine chromophores. Dependent on their local environment and structures, excited states of different energies are formed. This would explain not only the excitation

wavelength-dependent emission of **2** but also of (P4VP)Au(C $_6$ F $_5$). For **1**, the emissions which are based on metal-philic are obviously more intense dominating the emission spectrum and/or the aggregation by aurophilic interactions prevents the formation of emissive pyridine aggregates.

Conclusion

Au(I) and Zn(II) complexes containing the poly-dentate ligand poly(4-vinylpyridine) (P4VP) can be prepared by reaction between (Me $_2$ S)AuCl and ZnCl $_2$, respectively. In both cases, almost insoluble substances with empirical formulas (PVP)(AuCl) $_{0.4}$ and (PVP)(ZnCl $_2$) $_{0.7}$ are formed. Both materials feature luminescence upon excitation with UV light. Emissions of (P4VP)–AuCl are based on aurophilic interactions whereas for the (P4VP)–ZnCl $_2$ compound, an excitation wavelength-dependent emission band could be observed. The latter behavior can be explained by the formation of aggregated species with different excitation energies. The model compound, (Etpy)AuCl, is not engaged in aurophilic or π – π interactions in the solid state. It does not show photoluminescence.

Experimental

All solvents and other reagents were commercially obtained and used as received. (Me $_2$ S)AuCl were prepared according to a published procedure [55]. P4VP was obtained from Sigma–Aldrich with a molar mass of $M_n \approx 60,000$ g mol $^{-1}$. NMR spectra were recorded on an Avance DRX 300 (300 MHz) spectrometer, and ^1H shifts are reported in ppm relative to SiMe $_4$, with the residual signal of the deuterated solvent as internal reference. UV–Vis spectra were recorded on a Cary 300 Bio photometer. The emission spectra were recorded on a Horiba Jobin–Yvon Fluorolog-3 spectrofluorometer. All emission spectra were corrected for wavelength-dependent instrument and detector response.

Single-crystal structure analysis was carried out on a Bruker Smart X2S diffractometer with graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [56] and refined by full-matrix least-squares on F^2 (SHELXL-97) [57]. The H atoms were calculated geometrically, and a riding model was applied in the refinement process (Table 2). CCDC 1523478 and 1523479 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at <https://summary.ccdc.cam.ac.uk/structure-summary-form>. Mass spectra were collected on a Finnigan LCQ DecaXPPlus ion trap mass spectrometer with ESI ion source emission.

Fig. 5 Electronic spectra of **2** in solid state: **a** + **c** emission and excitation spectra at r.t. ($\lambda_{\text{exc}} = 310$ nm, $\lambda_{\text{det}} = 400$ nm) and **b** + **d** emission and excitation spectra at 77 K ($\lambda_{\text{exc}} = 320$ nm, $\lambda_{\text{det}} = 400$ nm)

Table 2 Crystal data and data collection and structure refinement details for **3** and **4**

Complex	3	4
Empirical formula	C ₇ H ₉ AuClN	C ₇ H ₉ AuCl ₃ N
<i>M_r</i> /g mol ⁻¹	339.57	410.47
Size/mm ³	0.50 × 0.32 × 0.07	0.32 × 0.44 × 0.09
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pcab</i>
<i>a</i> /Å	8.2208(9)	14.1898(12)
<i>b</i> /Å	5.2281(5)	7.9180(8)
<i>c</i> /Å	20.066(2)	19.2810(19)
<i>V</i> /Å ³	847.74(15)	2166.3(4)
ρ_{calcd} /g cm ⁻³	2.661	2.517
<i>Z</i>	4	8
<i>T</i> /K	300	300
θ range/°	2.5–30.2	2.6–23.3
Measured reflections	19,448	29,729
Independent reflections	2422	1590
Reflections with <i>I</i> > 2 σ (<i>I</i>)	1707	1361
Absorption correction	Multi-scan	Multi-scan
<i>T_{min}</i> / <i>T_{max}</i>	0.21/0.37	0.07/0.36
Restraints/refined param.	0/92	0/110
<i>R</i> ₁ (<i>I</i> ≥ 2 σ (<i>I</i>))	0.041	0.054
<i>wR</i> ₂	0.132	0.183
$\Delta\rho_{\text{fin}}$ (max/min)/e Å ⁻³	1.58/–1.34	2.68/–1.75
CCDC	1523478	1523479

Chlorido[poly(4-vinylpyridine)]gold(I), (P4VP)AuCl (1**, (C₇H₇N) AuCl)_{0.4}** An ethanolic solution of 17 mg poly(4-vinylpyridine) (0.17 mmol of pyridine groups) was added to 50 mg (Me₂S)AuCl (0.17 mmol) in 20 cm³ dichloromethane. A clear solution formed. After few minutes, a white precipitate was formed. The reaction mixture was stirred for additional 2 h at room temperature. The product was filtrated yielding a white powder. Yield: 38 mg (76%).

Dichlorido[poly(4-vinylpyridine)]zinc(II), (P4VP)ZnCl₂ (2**, (C₇H₇N) (ZnCl₂)_{0.7})** An ethanolic solution of 850 mg P4VP (8 mmol of pyridine groups) was added to 20 cm³ of an ethanolic solution of 220 mg ZnCl₂ (1.6 mmol). A clear solution formed. After few minutes, a white precipitate was formed. The reaction mixture was stirred for additional 2 h at room temperature. The product was filtrated yielding a white powder. Yield: 180 mg (46%).

Chlorido(4-ethylpyridine)gold(I), (4-Etpy)AuCl (3**, C₇H₉AuClN)** 4-Ethylpyridine (1.0 mmol, 0.11 g) was added to a dichloromethane solution (20 cm³) of 0.30 g (Me₂S)AuCl (1.0 mmol) and was stirred for 2 h at room temperature in the dark. After removing the solvent under vacuum, the residue was washed with diethyl ether to give a white

product. Recrystallization by slow diffusion of diethyl ether into DCM solution of **3** yielded crystals suitable for single-crystal X-ray diffraction. Yield: 200 mg (58.82%); ESI–MS (MeOH): *m/z* = 411.27 [(Etpy)₂Au]⁺; ¹H NMR (DMSO-*d*₆, 300 MHz): δ = 1.19 (3H, t), 2.71 (2H, q), 7.59 (2H, m), 8.67 (2H, m) ppm; UV–Vis (DCM): λ_{max} = 254 nm.

Trichlorido(4-ethylpyridine)gold(III), (4-Etpy)AuCl₃ (4**, C₇H₉AuCl₃N)** Some red crystals of **4** were formed in an attempt to recrystallize **3** from DCM/Et₂O. Also some purple precipitate was formed from the disproportionation reaction. The amount of **4** was not sufficient for a complete analysis. Besides single-crystal X-ray diffraction, an absorbance spectrum in DCM was recorded: UV–Vis (DCM): λ_{max} = 243, 316 nm.

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